REPORT DOCUMENTATION PAGE

AFRL-SR-AR-TR-03-

0246

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	24 June 2003	Final Report 6/15/01-12/31/02

4. TITLE AND SUBTITLE
Chemical Precursor Routes to Ceramic Nanocylinders

5. FUNDING NUMBERS
AFOSR Grant F49620-01-1-0443

6. AUTHOR(S)

Larry G. Sneddon

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

University of Pennsylvania
Department of Chemistry
231 South 34th Street
Philadelphia, PA 19104-6323

8. PERFORMING ORGANIZATION REPORT NUMBER

1-2003

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Office of Scientific Research
Ceramic and Non-Metallic Materials Program
801 N. Randolph Street, room 732
Arlington, VA 22203-1977

Dr. Joan Fuller, Manager

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT

Publicly Available

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 Words)*

The objective this AFOSR sponsored project was to design and synthesize new, processable chemical precursors to nonoxide ceramics that allow the formation of the ceramics in nano-structured forms. These studies demonstrated that the use of a suitably designed molecular or polymeric single-source precursor in conjunction with porous alumina nano-templating methods can be used for the systematic generation of aligned, monodispersed ensembles of boron carbide, boron nitride and silicon carbide ceramic nanocylinders. These methods should now be useful for the production of a wide range of nanostructured ceramics.

14. SUBJECT TERMS
ceramics, nanostructures, nanocylinders, nanotubes, boron carbide, boron nitride, silicon carbide

15. NUMBER OF PAGES
6

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	UL

RECEIVED JUL 0 9 2003

Summary of Major Research Accomplishments for:

Chemical Precursor Routes to Ceramic Nanocylinders

AFOSR GRANT F49620-01-1-0443

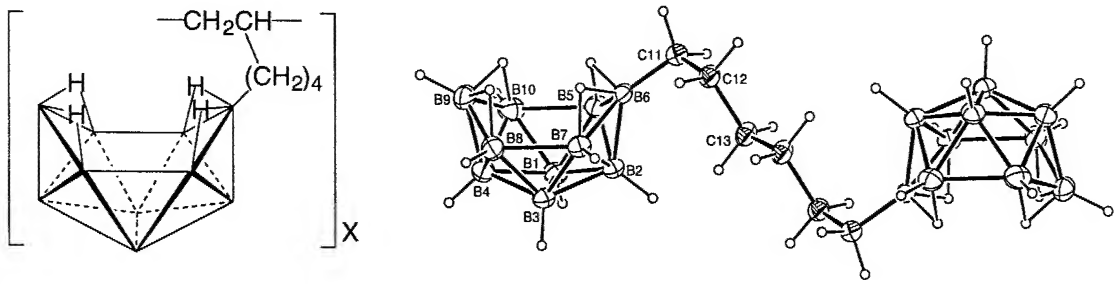
Larry G. Sneddon

Department of Chemistry
University of Pennsylvania

The objective of our recently completed AFOSR sponsored project was to design and synthesize new, processable chemical precursors to nonoxide ceramics that allow the formation of these materials in nanocylinderical (nanotubular) forms. Our studies that resulted in the formation of nanotubular boron carbide, boron nitride and silicon carbide ceramics are described in the following sections.

Boron Carbide and Boron Nitride Nanocylinders

We have previously shown that polyhexenyldecaborane and 6,6'-$(CH_2)_6$-$(B_{10}H_{13})_2$ (Figure 1) are both excellent precursors to boron carbide that yield carbon-rich (~B_4C) and boron-rich (~B_8C) boron carbide compositions, respectively.[1,2]



$[C_6H_{11}B_{10}H_{13}]_x$ 6,6'-$(CH_2)_6$-$(B_{10}H_{13})_2$

Figure 1. Polymeric and molecular precursors to boron carbide

We also demonstrated that boron carbide nanofibers can be produced via melt infiltration of 6,6'-$(CH_2)_6$-$(B_{10}H_{13})_2$ into porous alumina templates followed by pyrolysis and dissolution of the membranes.[2] Our AFOSR studies have found[3,4,5] that ceramic nanotubules can be generated by a procedure (Figure 2) similar to that reported by Martin[6] for the production of polymer nanotubes. Thus, by using precursor solutions, instead of neat liquid precursors, only the channel walls of the template were coated when these solutions were vacuum filtered through the membranes. Following pyrolysis and subsequent dissolution of the membranes, freestanding nanotubular boron carbide structures were produced.

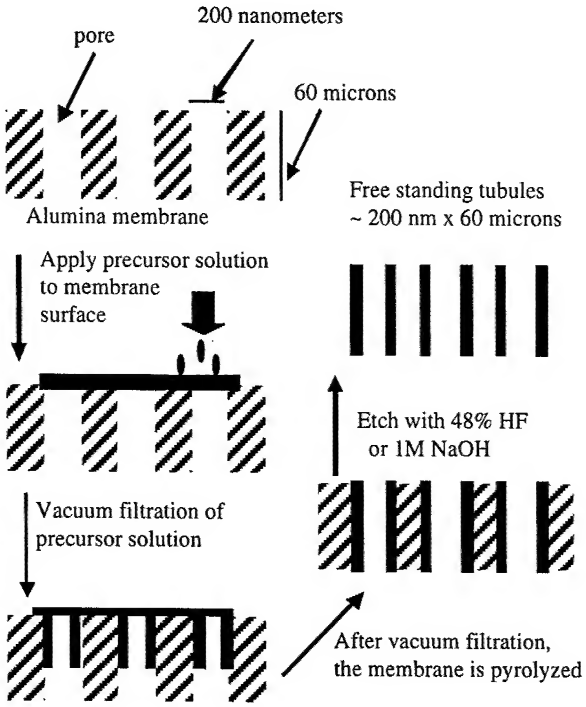


Figure 2. Nanotube Fabrication Method

The SEM image in Figure 3 shows an end view of an ensemble of boron carbide nanotubules that are ~50 μm long and ~250 nm in diameter. Both the SEM image in Figure 3 and the TEM image of a single nanocylinder in Figure 4, clearly show the hollow cores of the tubular structures. The inside diameter and wall thickness of the nanotubules can be controlled by the solution concentration and/or number of membrane treatments.

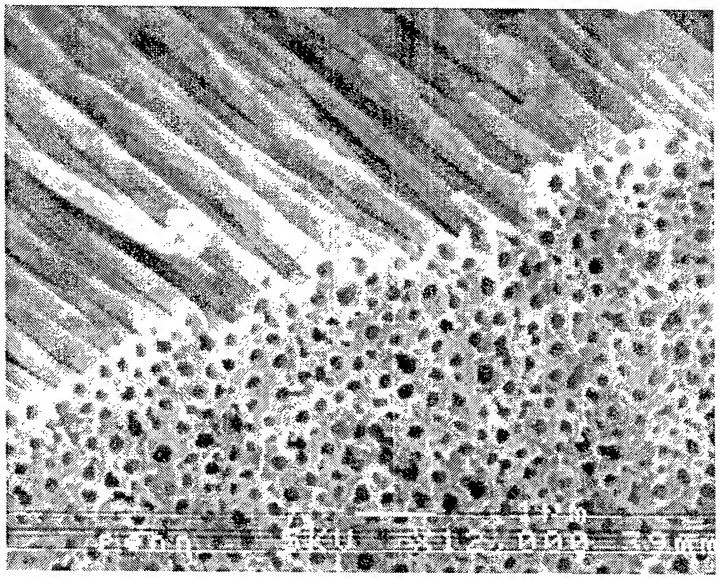


Figure 3. SEM image of boron carbide nanocylinders showing their hollow cores

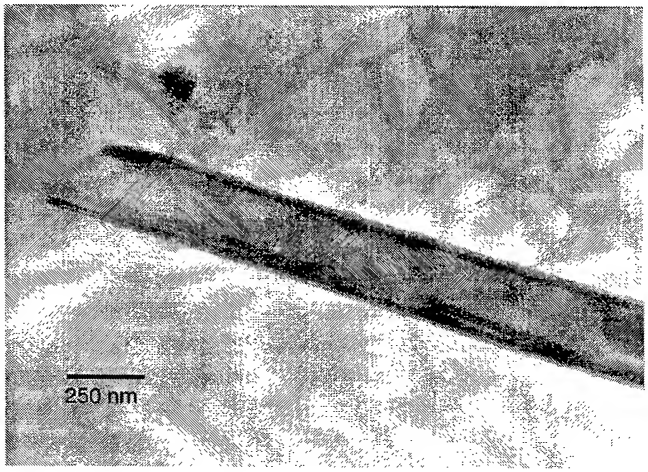


Figure 4. TEM image of a single boron carbide nanotubule

We have also now shown[4,5] that boron nitride nanotubules can be easily generated by employing our polyborazylene $(B_3N_3H_4)_x$ precursor[7] and the porous alumina templating technique. Thus, following the general procedure outlined in Figure 2, vacuum filtration of a polyborazylene solution through the alumina membranes followed by pyrolysis at 750°C and dissolution of the membranes in 1M NaOH yielded free-standing boron nitride nanotubules. As shown in Figure 5, SEM and TEM analyses confirmed the formation of an aligned ensemble of nanotubules.

Electron diffraction data obtained from these nanotubules (d = 3.43 Å [002], 2.07 Å [100], 1.24 Å [110]) were consistent with the formation of turbostratic boron nitride. Likewise, the electron energy loss spectrum (EELS) obtained from a single nanotubule was consistent with a boron nitride composition, showing the K-edges of boron at 190 eV and nitrogen at 400 eV.

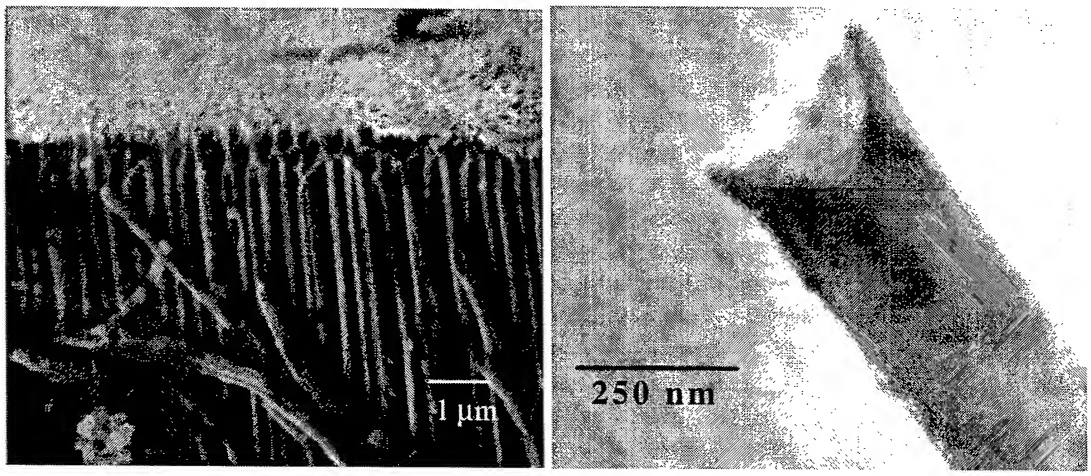


Figure 5. SEM and TEM images of an ensemble of boron nitride nanotubules (left) and a single boron nitride nanotubule (right).

SiliconCarbide Nanocylinders

Allylhydridopolycarbosilane (AHPCS) is a processible silicon carbide precursor that is manufactured by Starfire Systems, Inc.[8] Again following the procedure outlined in Figure 2, vacuum filtration of AHPCS solutions through alumina membranes followed by pyrolysis to 1025°C and subsequent dissolution of the membranes in 48% HF yielded silicon carbide nanotubules.[4,5] SEM (Figure 6) and TEM analyses confirm the formation of aligned silicon carbide nanotubular structures.

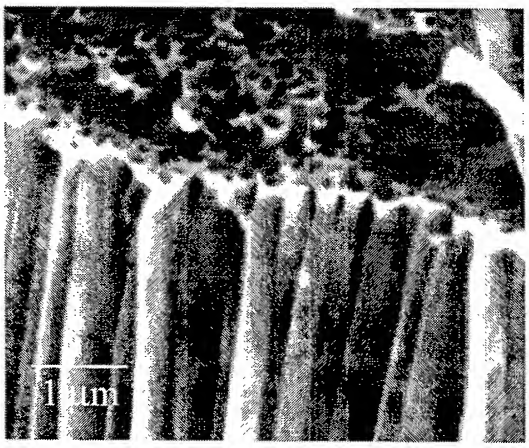


Figure 6. SEM image of an ensemble of silicon carbide nanotubules.

In conclusion, our work has shown that designed molecular and polymeric single-source precursors in conjunction with nano-templating methods enable the systematic generation of aligned, monodispersed ensembles of boron carbide, boron nitride, and silicon carbide nanotubules. We are now investigating the structural and electronic properties of these materials, as well as the use of these template methods for the production of a wide range of other nanostructured ceramics.

Publications resulting from the grant:

1. M. J. Pender, K. Forsthoefel and L. G. Sneddon, The Design, Syntheses and Applications of Group 13 Molecular and Polymeric Precursors to Advanced Ceramics, in Group 13 Chemistry: Fundamental Research, Materials Science and Catalysis, Shapiro, P. and Atwood, D. eds., American Chemical Society Symposium Series, ACS: Washington, D. C., 2002, 168-180.
2. K. M. Forsthoefel, M. J. Pender and L. G. Sneddon, Chemical Precursor Routes to Nanostructured Non-oxide Ceramics, Materials Research Society Proceedings, 2002, 53: 60-64.
3. A. R. Puerta, E. E. Remsen, M. G. Bradley, W. Sherwood and L. G. Sneddon, Synthesis and Ceramic Conversion Reactions of 9-BBN-Modified Allylhydridopolycarbosilane: A New Single-Source Precursor to Boron-Modified Silicon Carbide, *Chem. Mater.*, 2003, 15, 478-485.

4. M. J. Pender, K. M. Forsthoefel and L. G. Sneddon, Molecular and polymeric precursors to boron carbide nanofibers, nanocylinders and nanoporous ceramics, *Pure and Applied Chem.* accepted.